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Cryomilling of Thermoplastic Powder for Prepreg Applications

by Brian Parquette, Anit Giri, Daniel J. O'Brien, Sarah Brennan, Kyu Cho, and Jerome Tzeng

ARL-TR-6591 **September 2013**

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14. ABSTRACT
The U.S. Army uses thermoplastic (TP) polyetherimide (PEI) prepreg for the manufacture of high-performance composite tank ammunition components. To manufacture the material, manufacturers typically use powder coating, in which TP powder is electrostatically deposited onto a fiber tow. Powder size and distribution have been major factors that determine the quality of prepreg. Cryomilling offers a powerful approach to produce powders with small particle size in bulk quantities by mechanical milling of starting powders with large particle size in a cryogen, such as liquid nitrogen. In this work, starting with 350-μm powders, we use cryomilling to produce PEI powders suitable for prepregging with particle sizes of less than 20 μm. For size characterization of the powders, wet sieving was found to be the most effective technique. Using this method, we determined that a milling time of 8 h at 400 rpm is sufficient to yield approximately 70% by mass of particles under 20 μm.

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cryomilling, composite, prepreg, PEI

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1. Introduction

The U.S. Army uses thermoplastic polyetherimide (PEI) prepreg to manufacture high-performance composite tank ammunition components. The production of thermoplastic (TP) prepregs is often accomplished via hot melt or solution processing—techniques that can be expensive because of the limited solubility and/or high melting temperatures of TP resins. Because of the difficulties associated with these techniques, manufacturers also use powder coating, in which TP powder is electrostatically deposited onto a fiber tow (*1*). For this process, the powder size and distribution have been known to be the major factors that determine the quality of prepreg. In general, based on industrial experience, a small and uniform particle size (approximately 25 μm) is preferred. Therefore, in this work a cryomilling process for PEI powder was developed to meet the requirements of PEI prepreg manufacture.

Mechanical milling has been widely used to process ceramics and metals into powder form (*2–4*). However, this technique has not been used extensively to process polymer materials because of difficulties associated with the repeated fracturing and cold welding of particles, leading to a limit in minimum particle size. Shaw and Pan (*5*) explored mechanical milling as an approach for processing polymers (*6*) and found the technique efficient if the milling was performed at cryogenic temperature by cooling the milling vessel with a cryogen, such as liquid nitrogen. This technique, often referred to as cryomilling, enables manufacturers to form parts in any shape from polymer powders, avoiding difficulties such as high viscosity and insolubility associated with conventional processing techniques (*6*). Since its introduction, cryomilling has been used to produce powders of many different polymers and their mixtures as well as metal-polymer nanocomposites (*6–14*). In addition to simply cooling the milling vessel, cryomilling can also refer to a technique in which the starting powders are milled within the cryogenic medium with milling balls forming slurry during milling (*15*). The powders remain in intimate contact with the cryogenic liquid in this cryomilling process.

Successful production of polymer powders requires a processing study to determine optimum operating parameters (starting material to milling media mass ratio, milling intensity, etc.). In this research, PEI powder is produced via cryogenic milling over a range of processing parameters with the goal of minimizing processing time and enhancing yield of powders with particle sizes of 25 μm or less.

This report discusses the characterization of the PEI powders produced by cryomilling within liquid nitrogen. PEI particles were analyzed via optical and electron microscopy to assess particle morphology and size while sieve analyses were used to determine size distribution. The following sections describe the initial microscopy methods of measurement followed by two separate sieve analysis methods. The milling procedures determined to be best suited for this application are then presented.

2. Experimental

PEI starting powders, Ultem Resin 1010P, nominally 350 μm in diameter, were obtained from Sabic Innovative Plastics. The powders were milled within liquid nitrogen in a 1S Szegvari attritor (Union Process, Akron, OH) with 0.25-in-diameter stainless steel balls and a powder-to-ball ratio of 1:64. Figure 1 shows a schematic design and photo of a typical cryomill. Several batches of powder were produced at one of three milling intensities: 180, 300, and 400 rpm. For each batch, samples were removed periodically and were thoroughly characterized using a range of techniques: wet sieving, dry sieving, optical microscopy, scanning electron microscopy (SEM), and x-ray diffraction (XRD). Table 1 summarizes the milling parameters and characterization methods used for each specimen.

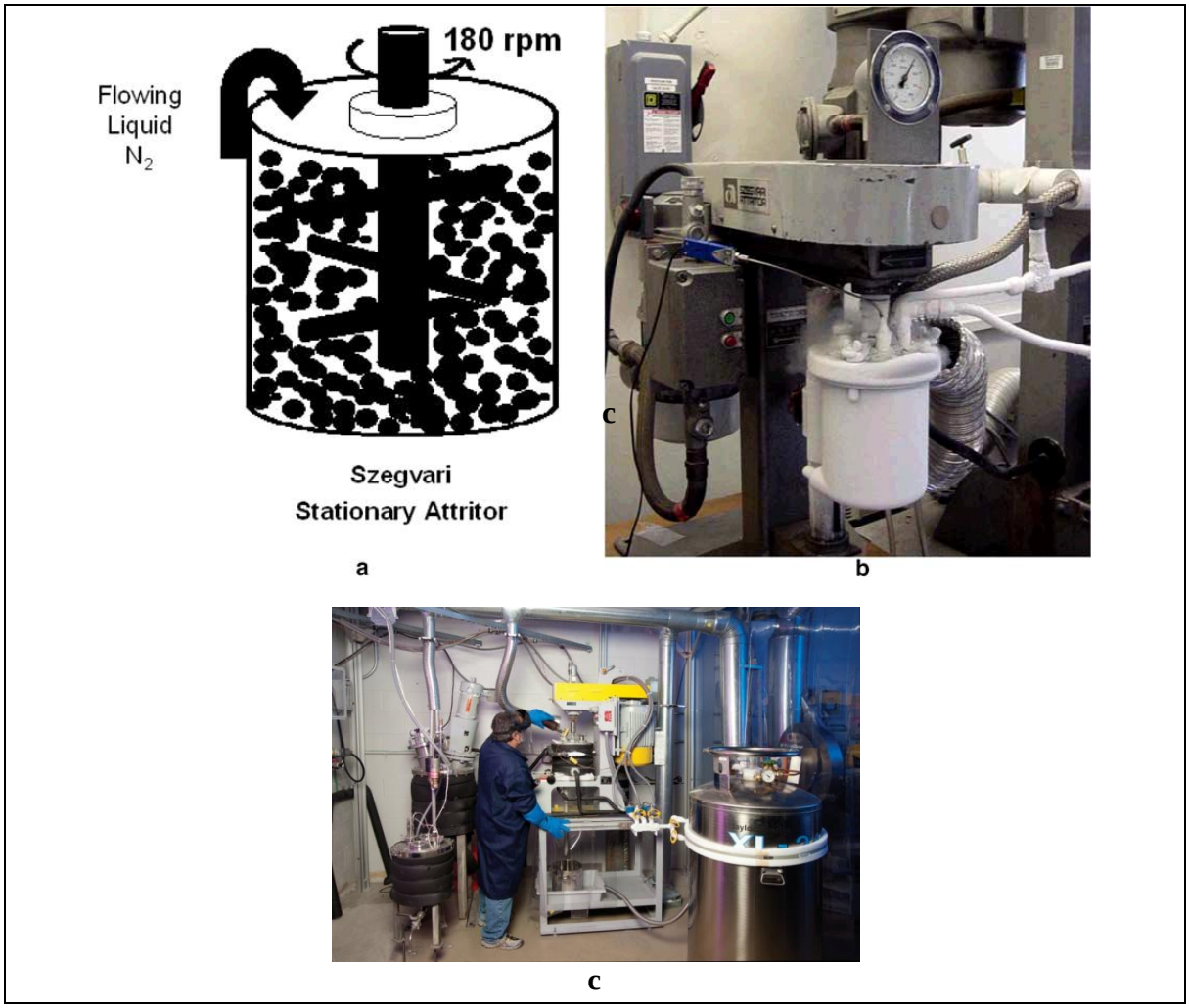

Figure 1. (a) Schematic design, (b) photograph of a typical cryomilling attritor mill (*15*), and (c) photograph of the U.S. Army Research Laboratory cryomilling system.

Table 1. Milling parameters and characterization techniques used for PEI powder specimens.

Specimen	Batch No.	Milling RPM	Milling Time	Dry Sieve	Wet Sieve	Optical Microscopy	SEM
Unmilled	NA	NA	NA	x	—	x	x
PEI-180-30 min	1	180	30 min	—	—	x	x
PEI-180-1 h	1	180	1 h	—	—	x	—
PEI-180-2 h	1	180	2 h	—	—	x	x
PEI-180-5 h	1	180	5 h	—	—	x	—
PEI-180-8 h	1	180	8 h	x	—	x	—
PEI-180-1 min	2	180	1 min	—	—	x	—
PEI-180-3 min	2	180	3 min	—	—	x	—
PEI-180-8 min	2	180	8 min	—	—	x	—
PEI-180-17 min	2	180	17 min	—	—	x	—
PEI-180-32 min	2	180	32 min	—	—	x	—
PEI-180-60 min	2	180	60 min	—	—	x	—
PEI-300-1 min	3	300	1 min	—	—	x	—
PEI-300-3 min	3	300	3 min	—	—	x	—
PEI-300-8 min	3	300	8 min	—	—	x	—
PEI-300-17 min	3	300	17 min	—	—	x	—
PEI-300-32 min	3	300	32 min	x	—	x	—
PEI-300-60 min	3	300	60 min	x	—	x	x
PEI-400-1 h	4	400	1 h	—	—	x	—
PEI-400-2 h	4	400	2 h	—	—	x	—
PEI-400-4 h	4	400	4 h	—	x	x	—
PEI-400-5 h	4	400	5 h	—	—	x	—
PEI-400-6 h	4	400	6 h	—	—	x	—
PEI-400-7 h	4	400	7 h	—	—	x	—
PEI-400-8 h	4	400	8 h	x	x	x	—
PEI-400-9 h	5	400	9 h	—	x	—	—
PEI-400-13 h	5	400	13 h	—	x	—	—

PEI particles were characterized via optical microscopy by placing a small amount of powder on a glass slide and separating the particles as best as possible. For some specimens, electron microscopy was additionally used to obtain higher-resolution images of the particles.

Both wet and dry sieving was performed using a set of stainless steel 8-in sieves (VWR Scientific, Batavia, IL) with sizes 425, 250, 150, 75, 45, and 20 μm, along with a solid pan placed below the bottommost sieve. For dry sieving, the sieves were stacked on a vibratory jogger (Model VJ, Cleveland Vibrator Co., Cleveland, OH) with the as-milled powder placed in the top sieve and vibrated for at least 5 h. For wet sieving, the sieves were once again stacked on top of the solid tray with the as-milled powder in the top sieve. The particles were saturated with ethanol while making a specific effort to break up large clumps and isolate the particles as much as possible. Once the particles appeared to be no longer flowing through the top sieve, it was lifted off the stack so ethanol could be sprayed onto the next smallest sieve, progressing down to the bottom of the stack. The sieves and slurry-filled bottom tray were then dried in an oven for at

least 4 h at 65 °C, leaving dried PEI particles behind. For both wet and dry methods, the sieves were weighed before and after processing with the difference taken as the mass of the particles captured by each sieve.

3. Results

3.1 XRD and Microscopy

Figure 2 shows the XRD patterns of the unmilled and 13-h cryomilled (PEI-400-13h) PEI powders. The patterns indicate the amorphous nature of the powders for both the samples. Figures 3–8 show optical micrographs of the powder as it progresses from the unmilled stage through each milling process, along with additional SEM images for 180- and 300-rpm milling speeds.

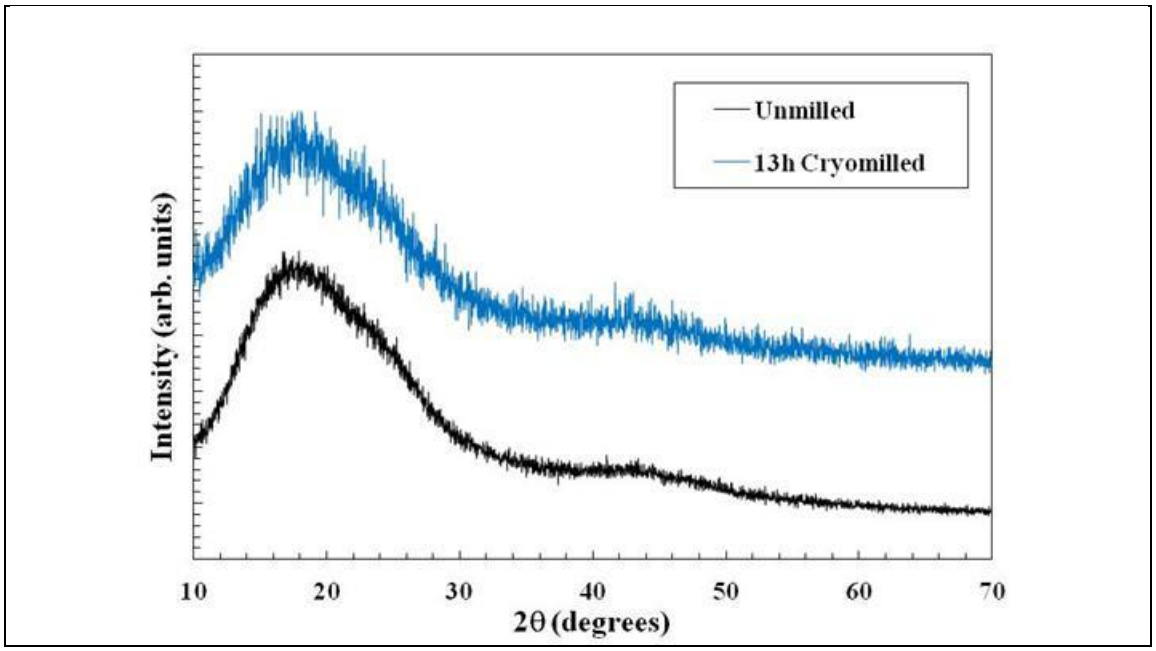

Figure 2. X-ray diffraction patterns of unmilled and cryomilled powders.

Figure 3 shows images of batch 1 milled at 180 rpm at various milling times from 0 to 8 h. As expected, the figure shows decreased particle size for advanced milling times. Most notably, the number of very small particles, under 20 μm, increases significantly above 2 h. However, the largest particles, approximately 500 μm, appear to persist at long milling times. It is unclear if the large particles present at long milling times are actually agglomerated small particles. Figure 4 shows SEM images of the same powders, similarly displaying an increase in the number of small particles with longer milling times but persistence of large particles.

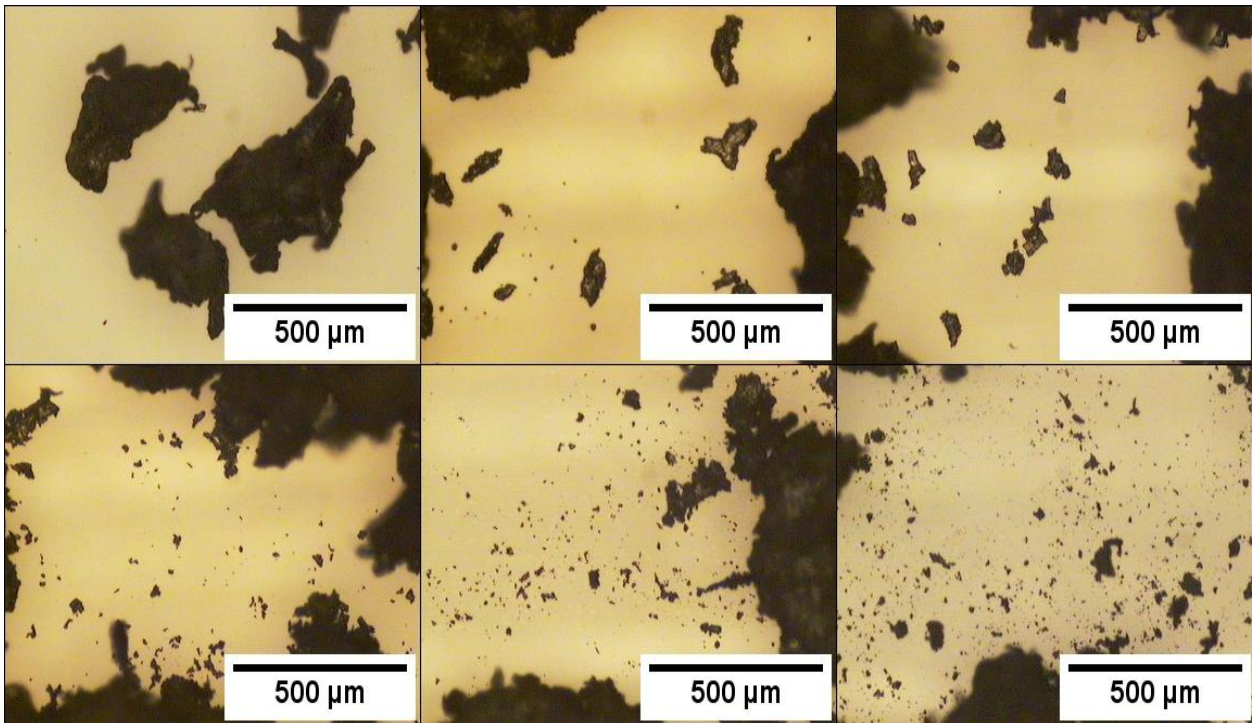

Figure 3. PEI powder from batch 1 milled at 180 rpm at milling times of (left to right, top row) 0, 0.5, and 1 h, and (left to right, bottom row) 2, 5, and 8 h.

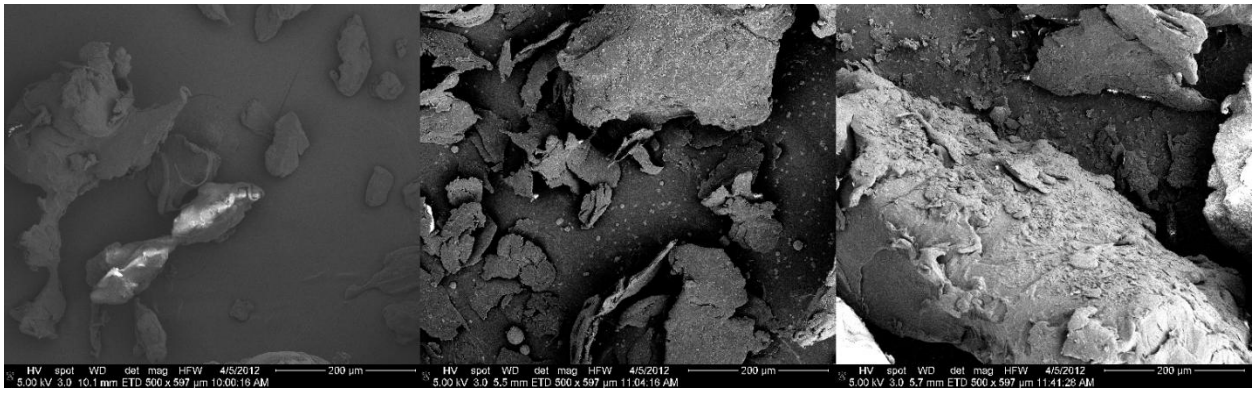

Figure 4. SEM images of PEI from batch 1 milled at 180 rpm at milling times of (left to right) 0, 30, and 60 min.

Figure 5 shows six images of batch 2 milled at 180 rpm. These images were all taken after relatively short milling times, less than 60 min, to explore the possibility that the average particle size passes through a minimum at short milling times before increasing because of agglomeration. However, no significant change in particle size was observed in these specimens.

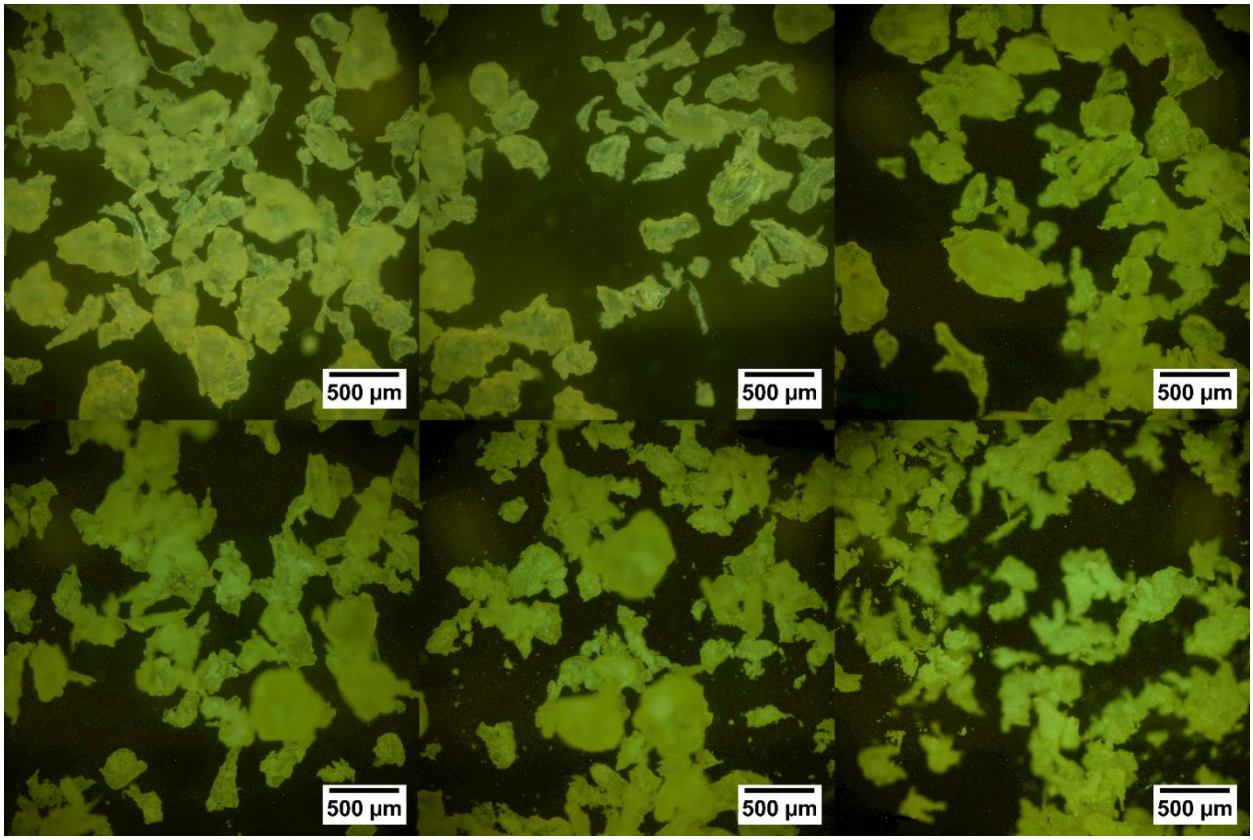

Figure 5. PEI powder from batch 2 milled at 180 rpm at milling times of (left to right, top row) 1, 3, and 8 min, and (left to right, bottom row) 17, 32, and 60 min.

Figure 6 shows images of batch 3 milled at 300 rpm for times between 1 and 60 min. Comparing the images from batch 3 to those of batch 2 taken at similar times (figure 5), we see that an increase in milling speed from 180 to 300 rpm has a significant impact on the size distribution of the resultant particles. Also, similar to batch 1, there is an increase in the number of very small particles but without the elimination of large particles. Figure 7 shows SEM images of the 60-min powder in this batch, again displaying both large and small particles present in the same specimen.

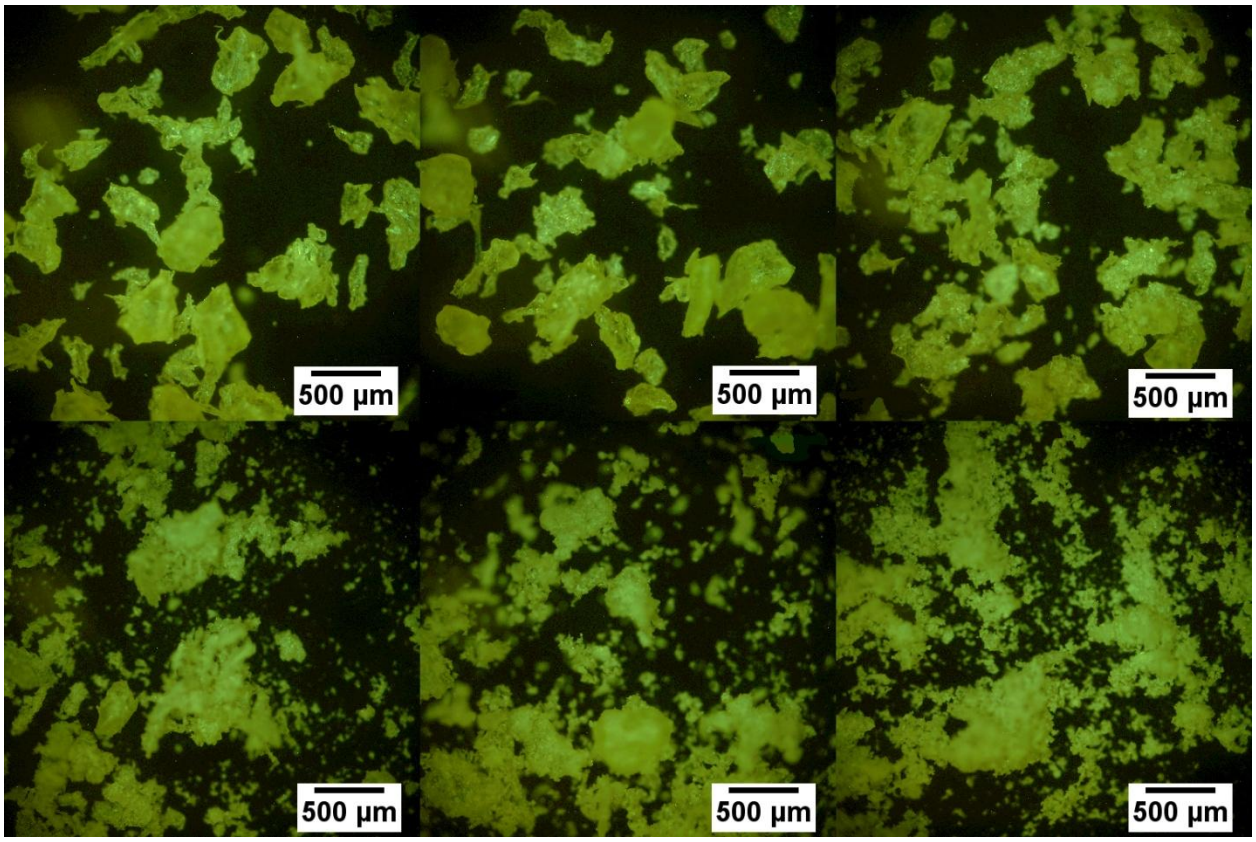

Figure 6. PEI powder from batch 3 milled at 300 rpm at milling times of (left to right, top row) 1, 3, and 8 min, and (left to right, bottom row) 17, 32, and 60 min.

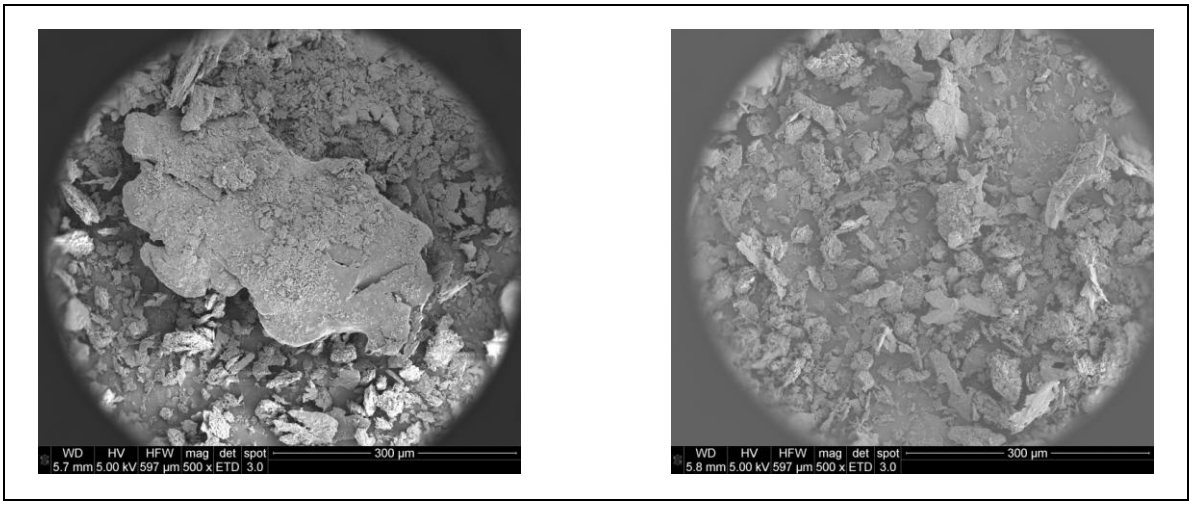

Figure 7. SEM images of PEI from batch 3 milled at 300 rpm for 1 h.

Figure 8 shows images of batch 4 milled at 400 rpm at various milling times. A similar pattern persists from the previous batches with a continued inability to discern if the large particles present at long milling times are agglomerated small particles.

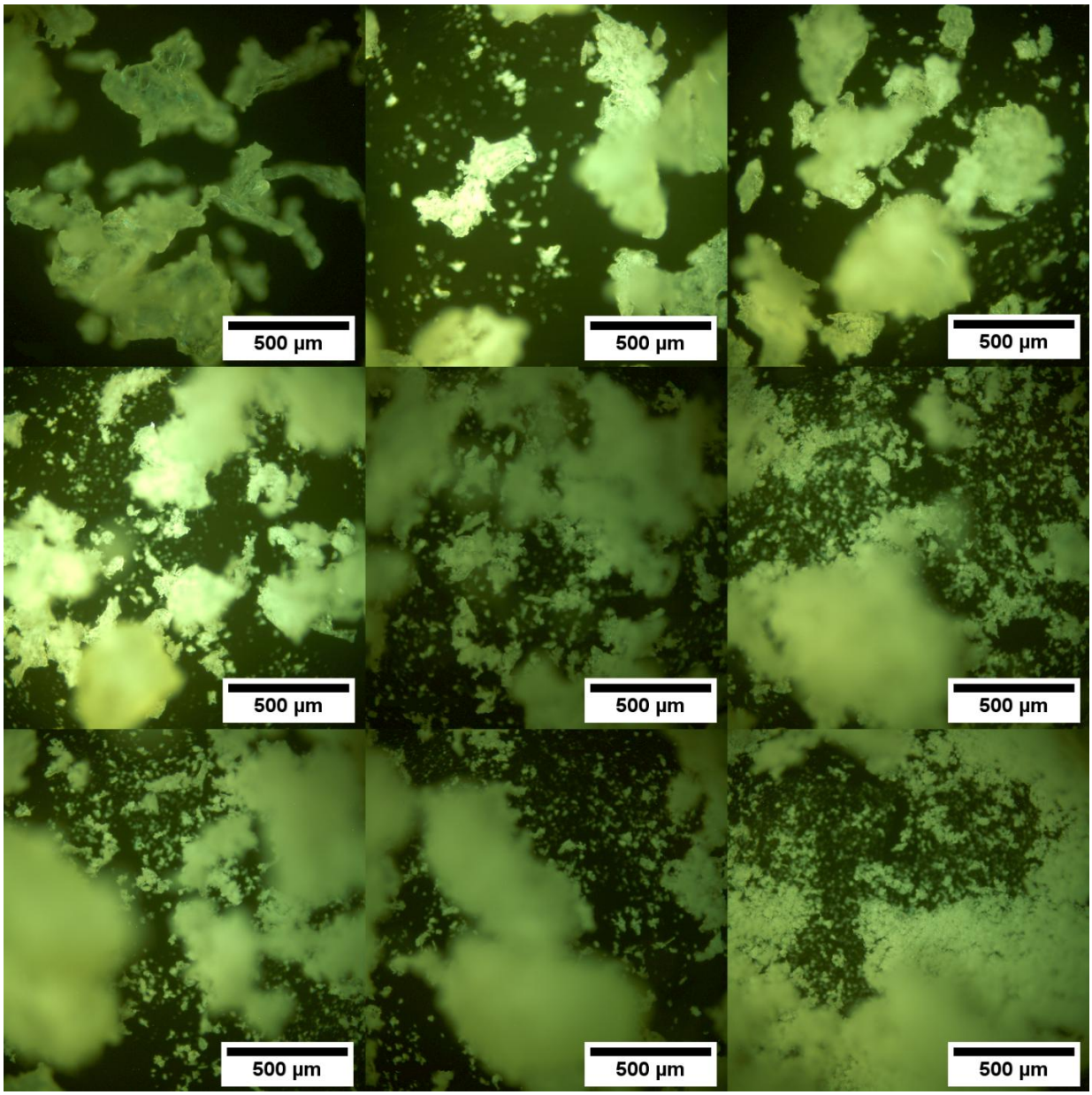

Figure 8. PEI powder from batch 4 milled at 400 rpm at milling times of (left to right, top row) 0, 1, and 2 h; (left to right, middle row) 3, 4, and 5 h; and (left to right, bottom row) 6, 7, and 8 h.

3.2 Dry and Wet Sieving

Particle size measurements obtained using the dry sieve process are shown in figure 9. For large particles, this process was effective and was used to make initial evaluations of the milling parameters. However, when smaller particles were sieved, their higher electrostatic attraction resulted in a caked layer of particles accumulated on top of a sieve that many of them would have otherwise passed through (figure 10). This caking behavior became most prevalent for sieve sizes below 250 µm. Furthermore, images taken after dry sieving show the relatively uniform size of particles collected in the 425-µm sieve (figure 11, left), while particles collected in the 45-µm sieve (figure 11, right) have a wide size distribution. These results suggest that dry sieving is not effective for separating PEI particles below approximately 250 µm.

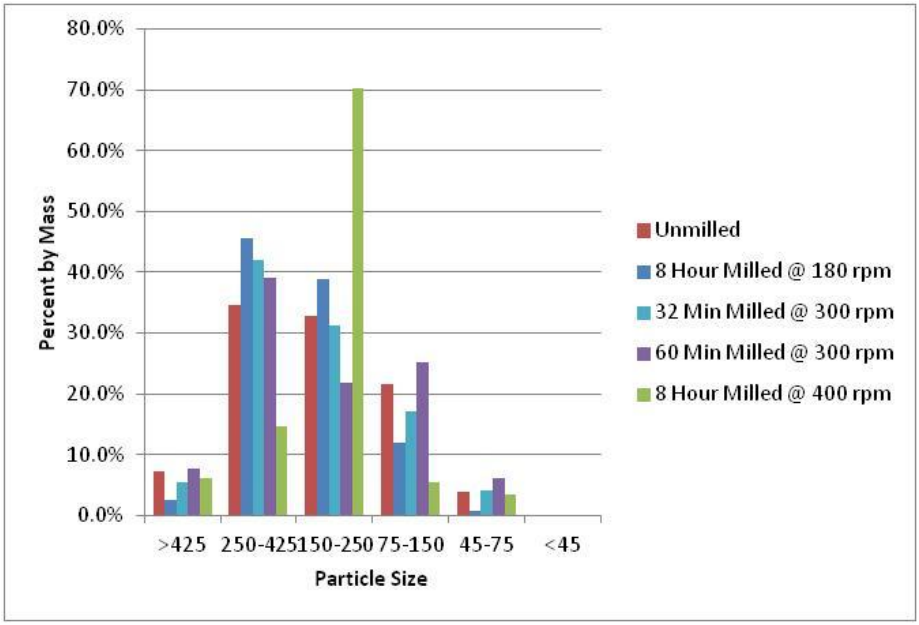

Figure 9. Size distribution measurements using dry sieve process.

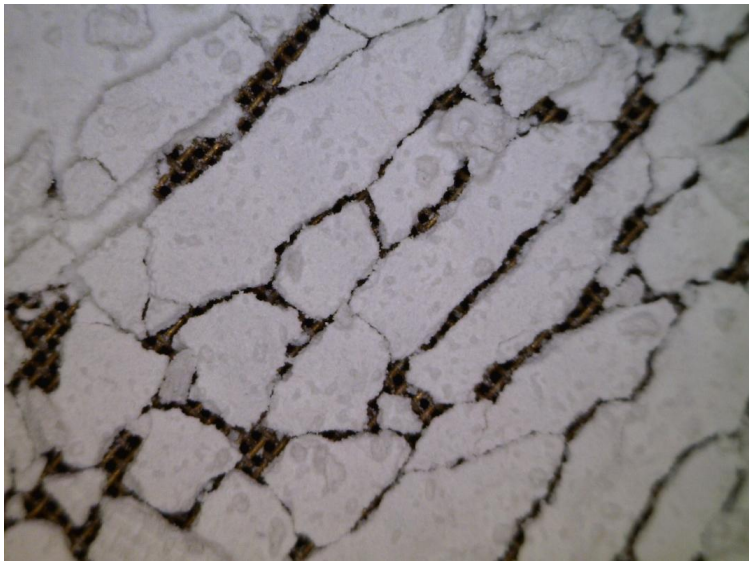

Figure 10. Small particles caked together during dry sieve process.

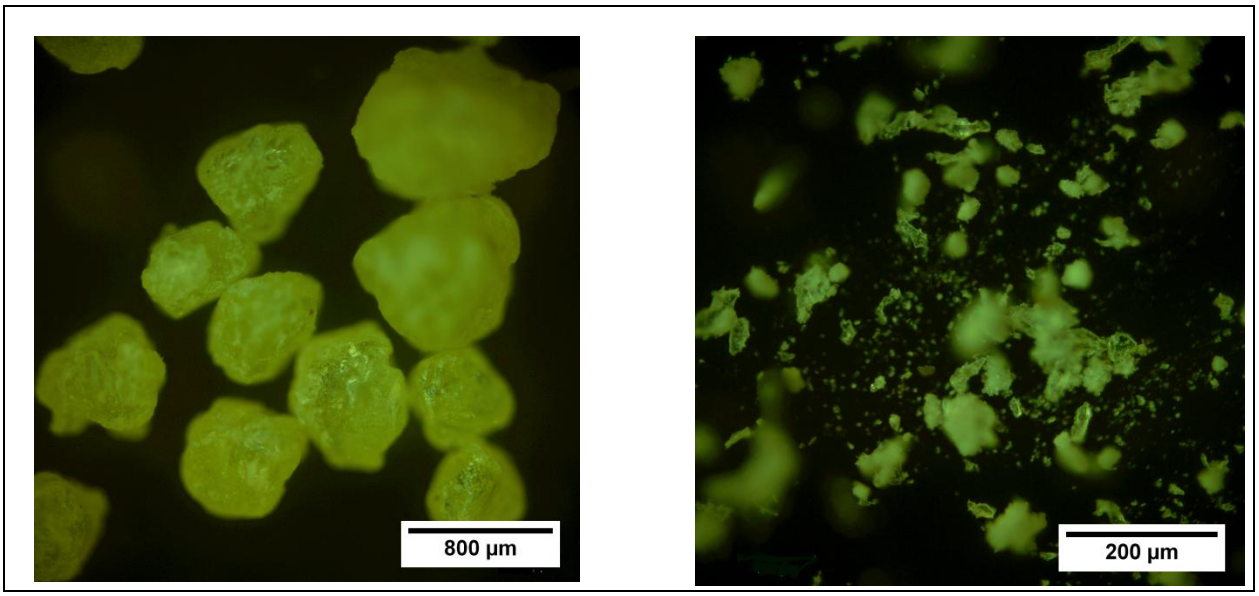

Figure 11. PEI-300 particles collected after dry sieving in 425-µm sieve (left) and 45-µm sieve (right).

Because of the agglomeration and caking observed during dry sieving, another technique is necessary for separating very small particles. Wet sieving in ethanol, as described previously, was used to analyze the size distribution of batches 4 and 5. The results are shown in figure 12. At 400 rpm, a milling time of 4 h produced particles mostly larger than 45 µm. At milling times of 8 h or longer, the dominant particle size decreases to below 20 µm.

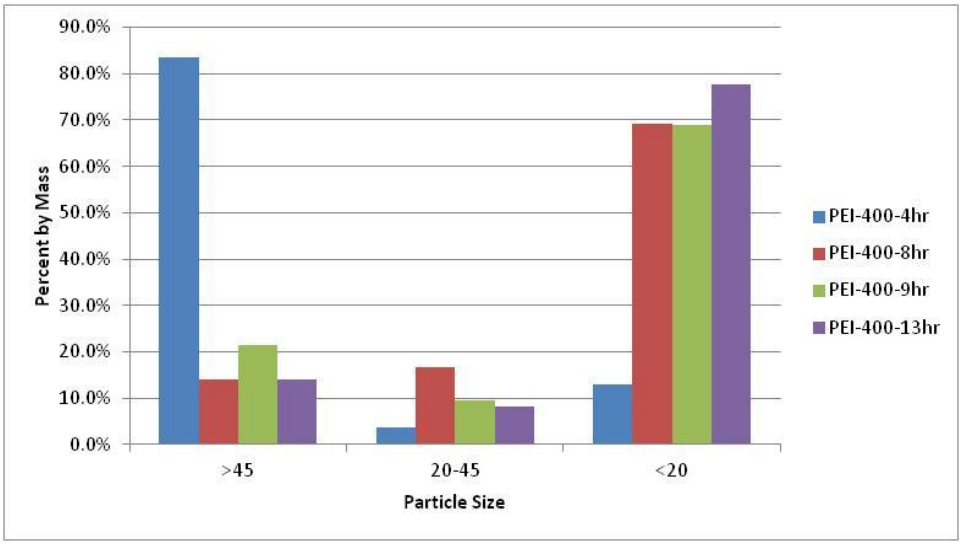

Figure 12. Size distribution measurements using wet sieve process.

4. Discussion

The microscopy images show that even for low milling speeds, there is a significant increase in the number of small particles. However, in every case, there still appears to be large masses, and from optical microscopy it was difficult to discern whether these were large particles or clumps of smaller particles. The SEM's better resolution made distinguishing the particle sizes easier, but the continued tight clustering of the particles made size measurement impractical.

The dry sieving process was effective for initial evaluation of milling parameters and was accurate for measuring large particles. Dry sieve measurements show a far greater milling effectiveness at higher speed, even for shorter milling times. However, for all five dry-sieved specimens, more than 50% of the particles (by mass) were larger than 150 μm and thus unsuitable for powder coating and necessitating higher milling speed and/or longer milling time. Furthermore, because of extensive caking in the sieve, dry sieving of the PEI-400-8 h sample indicated that none of the particles were smaller than 45 μm, while wet sieving showed that more than 85% of the particles (by mass) were smaller than 45 μm. These results clearly show that dry sieving is inappropriate for very small particles.

Wet sieving was able to more accurately determine size distribution for sub-100-μm particles and emerged as the most effective method of characterization. The measurements of powders milled at 400 rpm show that after 4 h, about 80% of the particles are still larger than 45 μm. Doubling the milling time to 8 h shrinks this figure down below 20%, and nearly 70% of the particles measure under 20 μm. Milling times longer than 8 h produce only marginally increased effectiveness.

5. Conclusions

We conducted this work to determine ideal milling parameters for producing fine PEI particles to use in powder-coated prepregs. We have verified that cryogenic ball milling is an efficient technique for producing fine powders for this purpose. For size characterization of the powders, wet sieving was found to be the most effective technique. Using this method, we determined that a milling time of 8 h at 400 rpm is sufficient to yield approximately 70% by mass of sub-2-μm particles. Although longer milling times produced continually smaller particles, the cost savings associated with a shorter processing time may outweigh the benefits of a finer powder. However, care must be taken during processing of these particles, as static charge becomes a significant factor at smaller particle sizes. Further experiments will include use of a compatible surfactant in order both to ensure uniform dispersion during processing and to test its effects on particle size during milling. Further work will also include the use of ceramic (e.g., tungsten carbide) milling balls and particle size characterization of larger-scale milling runs.

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